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Conversion of paper to film by ionic liquids: manufacturing process and properties

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KEYWORDS

Cellulose, dissolution, paper, ionic liquid, all-cellulose composite

ABSTRACT

In this study, we investigate the “chemical welding” of paper with the ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) using a two-step process. First, the IL is transported into the structure of the paper as a water solution. Then, partial dissolution is achieved by activation with heat, where the water evaporates and the surfaces of the fibres partially dissolve. The activated paper is washed with water to remove IL, and dried to fuse fibre surfaces into each other. The “chemically welded” paper structure has both elevated dry and wet strength. The treatment conditions can be adjusted to produce both paper-like materials and films. The most severe treatment conditions produce films that are fully transparent and their oxygen and grease

barrier properties are excellent. As an all-cellulose material, the “chemically welded” paper is fully biodegradable and is a potential alternative to fossil fuel-based plastics.

INTRODUCTION

The consumption of packaging materials has continuously been rising due to increased transportation of goods and food materials around the world, which has been steadily increased due to online shopping and offshoring of manufacturing plants.[1] This rise in material consumption has been met mainly by fossil fuel-based plastics and lignocellulose-based materials. Since packages are typically utilized only once, plastic materials, which have incomplete recycling cycles, cause environmental pollution, also harming animals and other living organisms, including, for example, human health issues related to the microplastics problem.[2] Consequently, the choice of packaging materials has been guided towards biodegradable, renewable materials. Thus, much of the growth in packaging material consumption has been covered by lignocellulosic materials, due to the renewability, recyclability, and abundance of wood fibre materials.[3] Among wood-based materials, cardboard, wrapping papers and films have been the most important materials used in packaging applications.

Wood fibres are mostly composed of cellulose, a linear polymer composed of glucose units connected by glycosidic bonds.[4] In paper and board, fibres are connected by interfibrillar hydrogen bonds forming layered sheets. Paper is strong when dry, but easily disintegrates in water, because water effectively breaks those bonds.[5] Therefore, in many paper applications, some wet strength additives are used to increase the water tolerance of paper via hydrophobization or forming chemical linkages between fibres.[5] Crystalline cellulose has an

inherent water resistance due to the tight orientation and packing of cellulose chains, which is utilized in regenerated cellulose films and filaments.[6] Regenerated cellulose materials are made by first dissolving cellulose in a suitable cellulose solvent system and then the dissolved cellulose is regenerated into a solid structure by using an antisolvent.[7] A large variety of the suitable non-derivatizing and derivatizing dissolution systems have been reported. Non-derivatizing direct dissolution chemistries such as cupro, NMMO·H_2O, and ILs are attractive since they do not alter the chemistry of cellulose, maintaining the excellent biodegradability of pure cellulose.[8–10] The most common process used to produce regenerated cellulose films is the cellophane process, where cellulose is regenerated from cellulose xanthate ("viscose") by dilute sulfuric acid; but greener alternatives such as novel ILs have been proposed.[11,12] These regenerated films have excellent mechanical properties, and due to their pure cellulose structure they maintain the natural hydrophilicity of cellulose. Recent developments have targeted combining regenerated cellulose with intact cellulose fibres to manufacture high-performance all-cellulose materials.[13,14] With this concept, no additives or coatings are required to achieve excellent mechanical properties both in a dry and wet state, which is combined with good barrier properties and excellent biodegradability.

All-cellulose materials can be made by using composite or partial dissolution approaches.[13] In the composite approach, cellulose fibres are embedded into a cellulose matrix, which is cast into the required shape, typically into a film. Comparatively, in partial dissolution, the premade paper is "chemically welded" by dissolving a thin layer on the fibre surface, allowing the fibre surfaces fuse together after regeneration. This approach has earlier been utilized with *N*-methylmorpholine-*N*-oxide (NMMO)[15], LiCl/DMAc[16], NaOH-urea[17], and ionic liquids[18]. In these

studies, pre-made paper sheets were directly immersed into the active dissolution solutions. The drawback of this approach is that if the cellulose solvent is viscous, dissolution mostly takes place only on the surfaces of the paper. We have shown that NMMO diluted with methanol can be utilized to more controllably "chemically weld" cellulose nanofibrils (CNF) film when the paper is first impregnated with NMMO in methanol, the methanol is evaporated off and the NMMO is activated with a hot calender.[19] The methanol for dilution has four functions: to lower the viscosity of cellulose solvent, to prevent dissolution of cellulose during the impregnation, to swell the paper structure in order to ease the permeation of the paper with the cellulose solvent, and to control the quantity of the active solvent added. The severity of the partial dissolution treatment can be controlled by the concentration of the cellulose solvent, treatment time and heat activation temperature. ILs have a special role in the preparation of all-lignocellulose material due to their claimed ability to dissolve all components of wood including cellulose, hemicellulose, lignin and even wood.[20] As an example, partial dissolution with 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) has been utilized to produce an all-wood-fibre composite from hinoki wood.[21] In the same study, cotton fabric was also transformed into a solid all-cellulose material. Havershals et al. studied the "chemical welding" of hemp and cotton yarns with [EMIM]OAc.[22] In that study, the yarns were placed in hot IL and then purified in water. The treatment causes gluing of the surface of yarns, and the toughness of the yarn was significantly increased. However, the authors present no industrially applicable conversion methods or attractive specified product applications.

In this study, pre-made paper sheets were treated with 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) diluted by water, followed by heat activation of the solvent in the oven. After

activation, the IL was removed from the paper by washing with water, and then the sheets were dried in an oven. Precipitation of the dissolved cellulose resulted in a fusion of the fibres of paper into a solid, uniform, high wet- and dry-strength material, with properties similar to thermoset plastics.

EXPERIMENTAL

MATERIALS

Bleached pine kraft pulp was obtained from a Finnish pulp mill. Laboratory handsheets (size 150 x 150 mm^2) with 100 g/m^2 (relative humidity (RH) 50%) grammage were prepared according to ISO standard 5269-1:05. 1-Ethyl-3-methylimidazolium acetate ([EMIM]OAc, purity 95%) was purchased from IoLiTec GmbH, Heilbronn, Germany. All other chemicals used in the study were of analytical grade. All water used in the study was purified with a Milli-Q device.

METHODS

Partial dissolution of paper sheets by ionic liquid

Partial dissolution of handsheets was carried out with 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc). [EMIM]OAc was diluted with water to 75 wt-% concentration before the treatment. Dry paper sheets were dipped into the [EMIM]OAc solution either for 15 s or for 3 min to change the absorbed volume of [EMIM]OAc-water in the paper sheet. Keeping the sheet in the solution for more than 3 minutes significantly weakened the paper sheet, leading to handling issues. Impregnated paper sheets were placed on a plate covered by aluminium foil and heated in the oven, where water quickly evaporated and the fibres then partially dissolved. A

series of samples (Figure 1) were prepared with varying oven temperatures and treatment times: (a) a reference without any treatment; (b) 15 s impregnation, oven 80 °C, treatment time of 50 min; (c) 3 min impregnation, 80 °C, 50 min; (d) 3 min impregnation, 95 °C, 50 min; (e) 3 min impregnation, 95 °C, 16 h. The heat-treated paper sheets carrying [EMIM]OAc on aluminium foil were then placed into water. Water was changed four times to wash out completely all the remaining ionic liquid. Aluminium foil was carefully peeled from the treated sheet after the first rinsing. The rinsed sheets were then wet-pressed at 3.5 bar for 5 minutes (ISO 5269-1:05) and dried with a L&W Rapid Dryer (ABB Ab / Lorentzen & Wettre) at 135 °C for 5 minutes. Dried sheets were stored at the standard thermo- and hygrostated conditions of 23 °C and 50% RH.

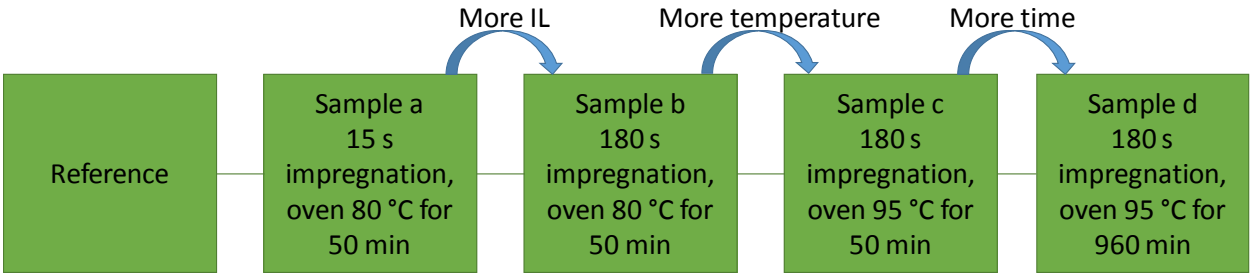


Figure 1. Optimization scheme for a partial dissolution process with [EMIM]OAc-water. The impregnation and heat activation conditions are shown in the boxes. The arrows on the boxes show the optimization steps.

Viscosity of aqueous IL solutions

The shear viscosity of IL-water solutions at concentrations of 100%, 90%, 75% and 50% were measured using a rotational rheometer (Anton Paar Rheometer MCR301) with TruGap™ measurement geometry. The sample was placed between a fixed bottom plate and a moving upper cone with the gap at 0.051 mm. The upper cone geometry was CP50-2, i.e. diameter 50 mm and cone angle 2°. Temperature was precisely controlled at 23 °C. Viscosity was measured at three shear rates: 10, 100, and 500 1/s.

Microscopy analyses

Scanning electron microscopy (SEM) imaging was carried out with a Merlin Field Emission (FE)-SEM (Carl Zeiss NTS GmbH, Germany) with applied gold sputter coatings (30 mA, 30 s). The electron gun voltage was a constant 3 kV with a grid current of 60 pA. The pixel resolution was 2048 x 1536.

Chemical analyses of IL-treated papers by solid state ^{13}C CP/MAS NMR spectrometry

Changes in the crystallinity of the wood fibres after [EMIM]OAc treatment were characterized by using a ^{13}C cross polarization magic angle spinning (CP-MAS) NMR spectrometer (Bruker AVANCE-III 400 MHz, Bruker BioSpin, Germany). For all samples, 20,000 scans were collected using an 8 kHz spinning frequency, 2-ms contact time, and a 5-second delay between pulses.

Mechanical properties of "chemically welded" papers

The apparent bulk density of the paper sheets with and without IL treatment was measured in accordance with ISO 5270:12, ISO 534:05. Gurley air resistance was measured in accordance with ISO 5270:12, ISO 5636-5:13. Tensile strength, tensile index, stretch at break, tensile energy absorption, TEA index, and tensile stiffness were measured in accordance with ISO 5270:12, ISO 1924-2:08. Tear strength was measured in accordance with ISO 5270:12, ISO 1974:12. Internal bonding strength (Scott bond) was measured in accordance with TAPPI T569:00. Wet tensile strength was measured at 10 min and 24 h immersion times in accordance with ISO 3781:11, SCAN-P 20:95.

Barrier properties

Air permeabilities of the samples were investigated using an L&W Air Permeance Tester, in accordance with ISO 5636-3:2013(E) Part 3: Bendtsen method. Measurements were repeated at least five times.

Water vapour permeabilities of the samples were determined gravimetrically using a modified ASTM-E-96B procedure "wet cup method". Samples with a test area of 30 cm^2 were mounted on circular aluminium cups (68-3000 Vapometer EZ-Cups; Thwing-Albert Instrument Company) containing distilled water (100% RH). The cups were stored in test conditions of 23 °C and 50% RH and weighed periodically until a constant rate of weight reduction was attained. Two parallel measurements were carried out. Results were normalized by the film thickness (in µm).

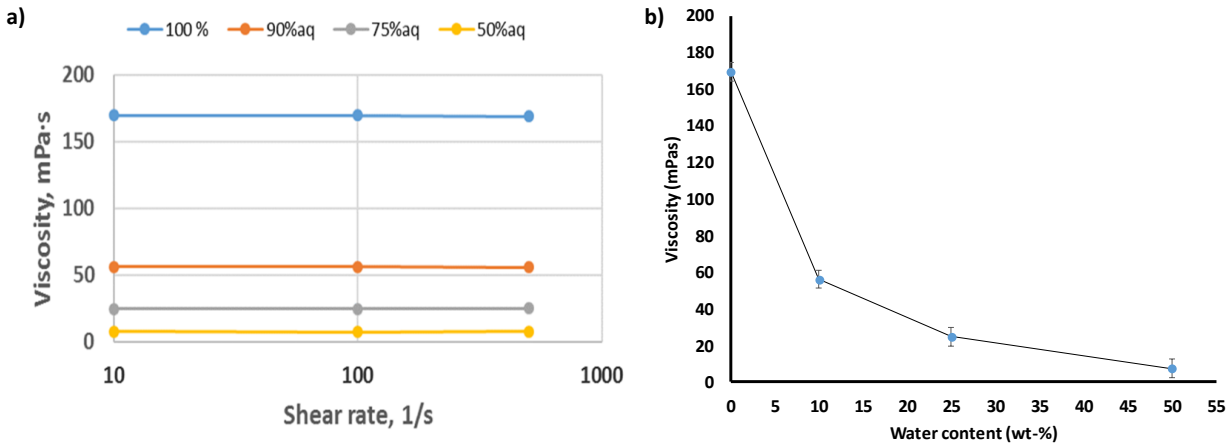
Oxygen permeabilities through the films were determined according to standard ASTM D3985 using an Oxygen Permeation Analyser Model 8001 (Systech Instruments Ltd, UK). Tests were carried out at 23 °C and 0% and 80% RH using 100% oxygen as a test gas. Two parallel measurements were carried out. Results were normalized by the film thickness (in µm).

Grease barrier properties were evaluated according to the method reported by Vähä-Nissi (2016). The paper sheets with the size of 50 mm x 50 mm were placed on a transparent glass plate. The sample (same size) was put on it. A circular blotting paper (diameter 30 mm) was further put on the sample, and 200 µl of "Oil Red O" (1-([4-(xylylazo)xylyl]azo)-2-naphthol, 1-[2,5-dimethyl-4-(2,5-dimethylphenylazo)phenylazo]-2-naphthol, Solvent Red 27, Sigma-Aldrich) dyed oil was pipetted onto the blotting paper. Then a 50-g weight (diameter 30 mm) was placed onto the blotting paper. Penetration of grease through the sample was detected by an image scanner (300 dpi, 24-bit colour) through the glass plate. 5 parallel measurements were carried out for 148 h with periodic image scanning.

RESULTS

Processing paper sheets with aqueous IL solution

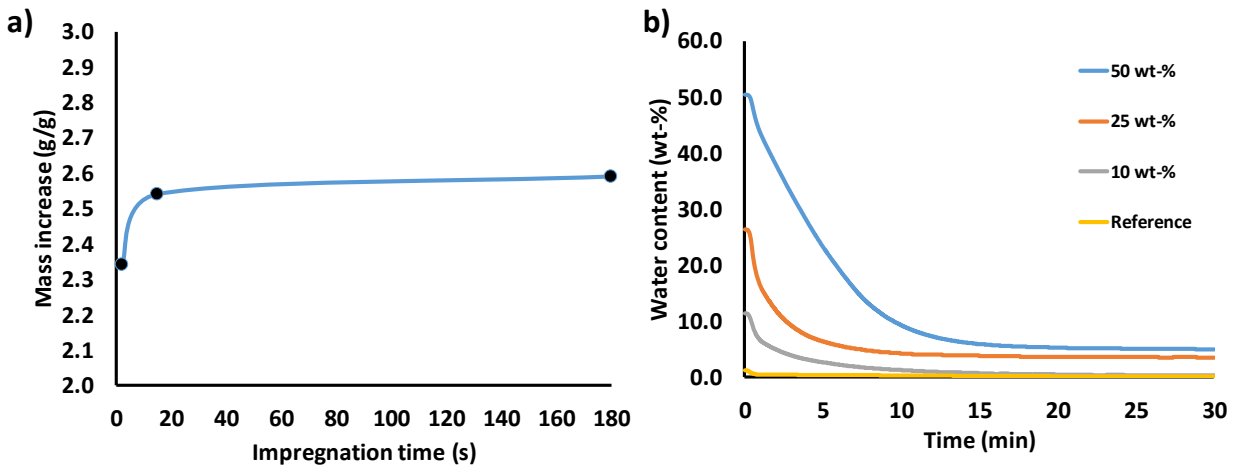
The paper samples were treated with the IL-water solution before heat activation in an oven. The role of the water in IL was to decrease the viscosity of the IL and swell paper so that the IL can better penetrate into its structure. Pure [EMIM]OAc with and without added water behaved as a Newtonian fluid without the shear rate response (Figure 2a). The viscosity of the pure [EMIM]OAc was 169.5 mPa·s (Figure 2b). When a 10 wt-% of water (water in IL mole ratio 1.1) was added, the viscosity decreased to 56.1 mPa·s. The higher water content, 25 (mole ratio 3.2) and 50 (mole ratio 10) wt-%, further decreased the viscosity value to 24.8 and 7.4 mPa·s, respectively. This explains that with a small water addition, the viscosity of [EMIM]OAc can be drastically decreased, easing processing. The observed viscosity decrease as a function of added water content was the same as reported earlier.[23] The viscosity of the pure [EMIM]OAc has also a strong temperature dependence. However, if the temperature is used to decrease the viscosity of IL, the dissolution reaction propagates simultaneously.[20] In this study, we did not investigate temperature dependence, because the aim of our procedure was to prevent dissolution during the impregnation phase in order to enhance the controllability of the treatment process.



181

182 *Figure 2. a) Viscosity of [EMIM]OAc with and without water as a function of shear rate at 20 °C. b) Viscosity*
183 *of [EMIM]OAc as a function of water content.*

184 The amount of [EMIM]OAc in the paper could be controlled with the dilution of the IL and the
185 impregnation time. The mass increase of the paper sheets during impregnation with a 75 w-%
186 [EMIM]OAc solution was estimated gravimetrically (Figure 3a). The impregnation process of the
187 paper is rapid, and the plateau was reached after 30 s impregnation time. After 15 s the mass
188 increase was approximately 2.5 g/g. After 30 s the mass did not significantly increase. From the
189 processability point of view, this is good because the treatment time is short. In this, the process
190 is analogous to surface sizing and chemical impregnation, which are common processes used in
191 the paper industry to enhance the permanence of paper.[24] Besides IL concentration, the
192 impregnation rate is influenced by the type of the cellulose fibres used and paper density.



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194 *Figure 3. a) Liquid uptake of the paper sheet as a function of time. b) Evaporation of the water from the*
195 *paper sheet treated with [EMIM]OAc-water solution with a water content range of 0–50 wt-% as a function*
196 *of heating time. Temperature was set to 95 °C.*

197 Water prevents the dissolution of cellulose by [EMIM]OAc. However, [EMIM]OAc is a special case
198 among ionic liquids because it can tolerate water: it can dissolve microcrystalline cellulose (MCC)
199 with water contents as high as 15 w-%.[25] Water tolerance is desirable for a cellulose solvent,
200 because water can be tightly bound to the IL and be difficult to completely remove by
201 evaporation at atmospheric pressure.[26] The rate of water evaporation from [EMIM]OAc at 95 °C
202 was estimated with a gravimetric moisture analyser at water contents of 0, 10, 25, 50 wt-%
203 (Figure 3b). For 25 m-% and above, mass loss was exponential, while for 50 m-%, it was partially
204 linear. A plateau below 10 m-%, sufficiently low to dissolve cellulose, was reached in all cases
205 after a 15-min heating time. Partial dissolution and diffusion of cellulose molecules begins only
206 after evaporation is complete. This quantitative result confirms the visual observation that water
207 is quickly evaporated from the tested paper samples in the oven.

208 **Partial dissolution of paper with the IL-water system**

209 The procedure used caused a controlled transformation of paper to permanent solid structures
210 (Figure 4). Visually, when treatment conditions were more severe, the transparency of the paper
211 increased. The sample treated with the mildest treatment (Sample a, Figure 1) still had a paper-
212 like feel and appearance (Figure 4b), but when the impregnated amount of the IL-water was
213 increased at a constant heating temperature (sample b), the transparency of paper increased
214 significantly (Figure 4c). In the most severe treatment conditions (samples c and d), paper
215 achieves a fully transparent structure (Figure 4d and e), and these samples resemble plastic films.
216 Moreover, the paper shrinks during treatment and drying, causing a remarkable increase of the
217 apparent density of paper samples as a function treatment severity (Table 1). The evaporation of
218 the water from the film structure causes the compaction of the film, which leads also to the
219 vanishing of the pores and voids when the fibrillar structure is lost.[27] The apparent sheet density
220 of the samples increases from 557 ± 16 kg/m^3 (reference) up to 1192 ± 167 kg/m^3 (sample 4), and
221 simultaneously the paper is transformed into transparent film. The IL treatment of paper with
222 [BMIM]Cl has been studied earlier elsewhere.[28] In the given study the paper sheets were treated
223 by direct immersion in hot [BMIM]Cl. This treatment resulted in only a change of visual
224 appearance because only the surface of the paper was treated.

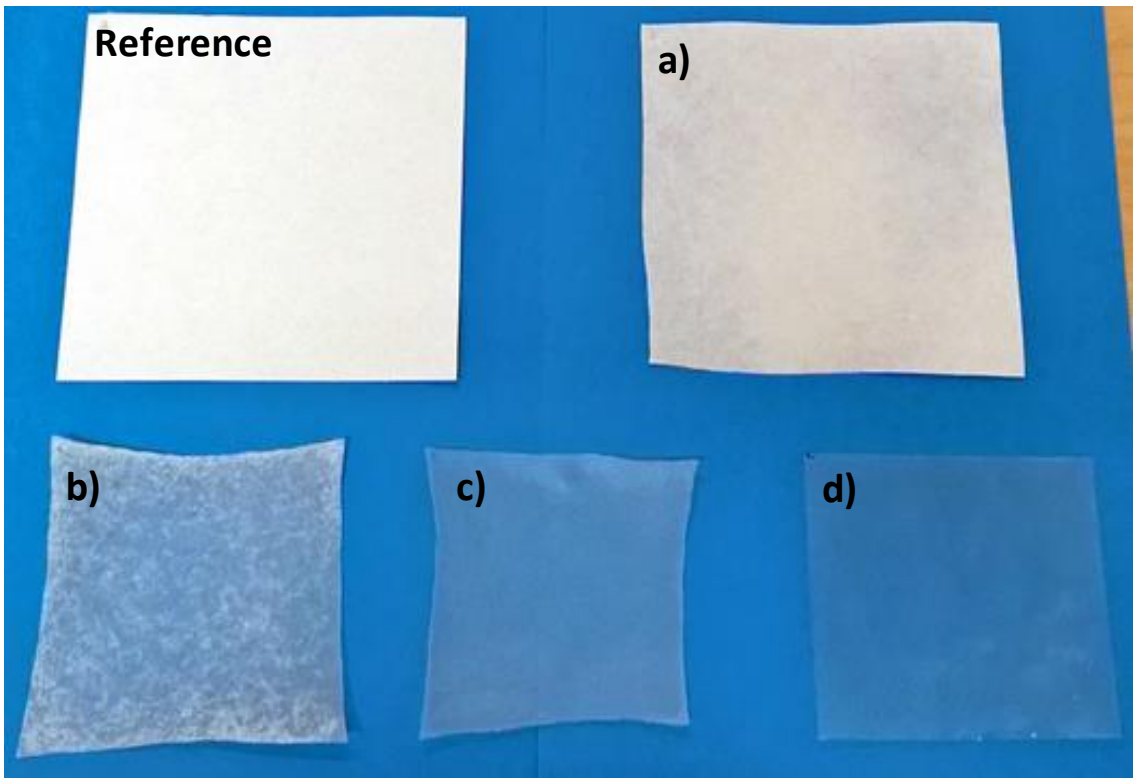
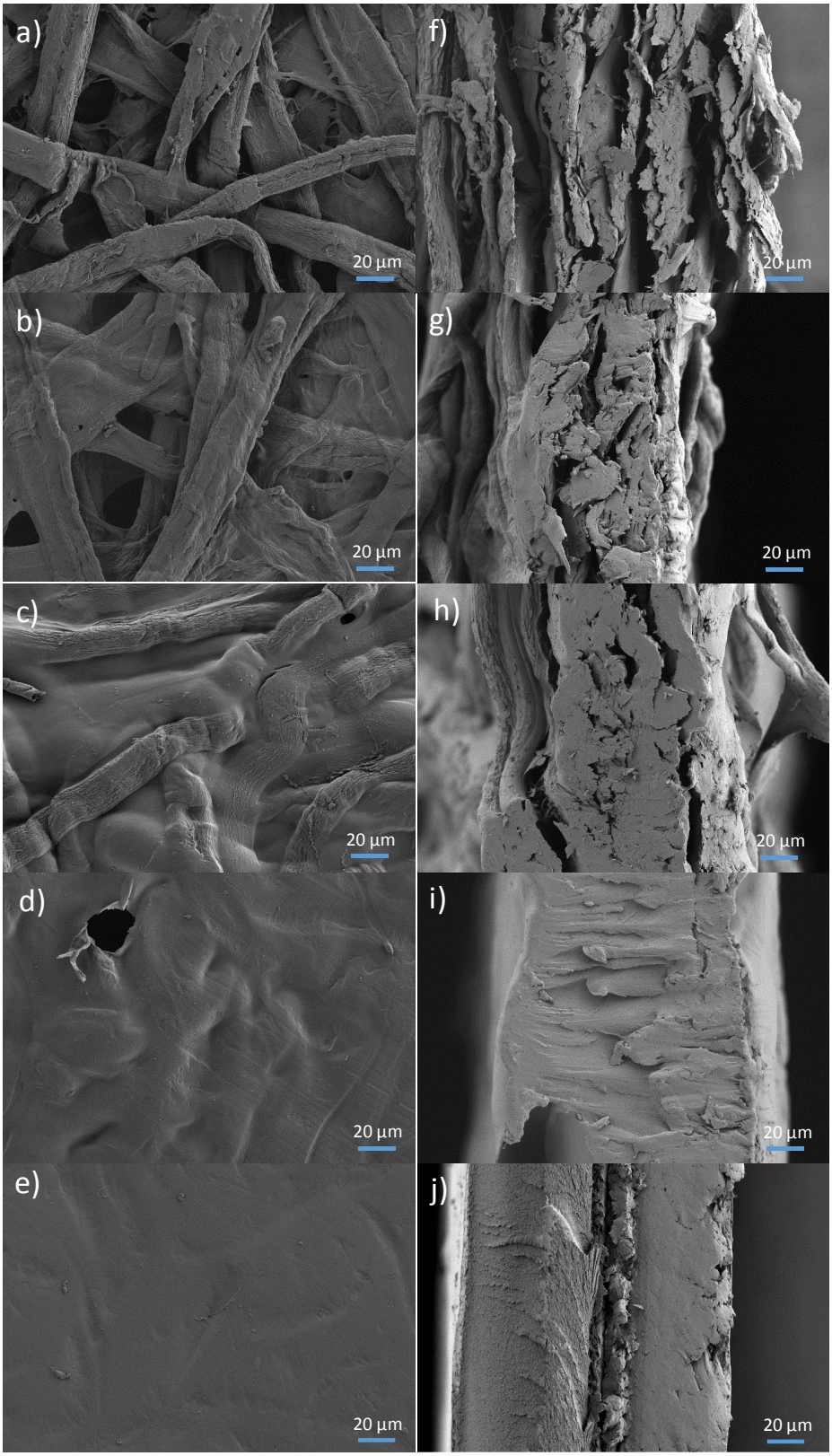


Figure 4. Series of ionic liquid-treated sheets in dry state: (a) Original handsheet; (b) Sample a; (c) Sample b; (d) Sample c; and (e) Sample d.

In scanning electron microscopy (SEM), the reference sample shows a fibre structure typical for regular paper (Figure 5a). Already the mildest IL treatment (sample a) caused the fibres to bind together tightly (Figure 5b). When the volume of the IL in the paper was increased with a longer impregnation time (sample b), the structure of the fibre was loosened and fibres were mobilized (Figure 5c). A higher activation temperature (sample c) caused the partial dissolution of the fibres, and they were embedded into a regenerated cellulose matrix (Figure 5d). The sample contained also some air bubbles that were mostly formed by the evaporation of the water. Heat activation overnight, for 960 min (sample d), caused full dissolution of the paper's fibrillar structure (Figure 5e). Cross-sectional images verify the same observations (Figure 5f-j). With this

238 long treatment time, the dissolved cellulose on the fibre surface had enough time to diffuse and
239 flow into a solid shape. Mild treatments retained the fibre structure mostly intact (sample a and
240 b), but in severe treatment conditions (sample c and d), the transparency of the paper was
241 increased and the fibrillar structure vanished.


a)
20 µm
f)
20 µm
b)
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g)
20 µm
c)
20 µm
h)
20 µm
d)
20 µm
i)
20 µm
e)
20 µm
j)
20 µm

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Figure 5. Scanning electron microscopy (SEM) images of surface and cross-section of the IL-treated sheets. a,f) Reference paper, b,g) sample a, c,h) sample b, c,h) sample c, d,i) sample d, and e,j) sample e.

^{13}C CP/MAS NMR spectroscopy is an established tool used to distinguish between cellulose I and II polymorphs. [29,30] As expected, the reference paper consisted of crystalline cellulose I and non-crystalline cellulose. After the mildest treatment (sample a), small changes in the NMR spectrum were observed indicating the formation of cellulose II (C6 moved to lower chemical shift) and loss of cellulose I structure (a decrease in the intensity of the crystalline C4 peak). In sample b, the change from the cellulose I to the cellulose II crystalline form was more drastic, but clearly there was still some cellulose I signal left. In the spectrum of sample c, the cellulose I signal vanished and was entirely replaced by the cellulose II signal. Treatment of wood pulp with *N*-methyl morpholine-*N*-oxide (NMMO) has been studied earlier,[31] and similar changes in the NMR spectrum were observed. The NMR results are in accordance with the visual (Figure 4) and SEM (Figure 5) characterizations: the paper became transparent, and simultaneously the fibrillar structure of the paper partially dissolved.

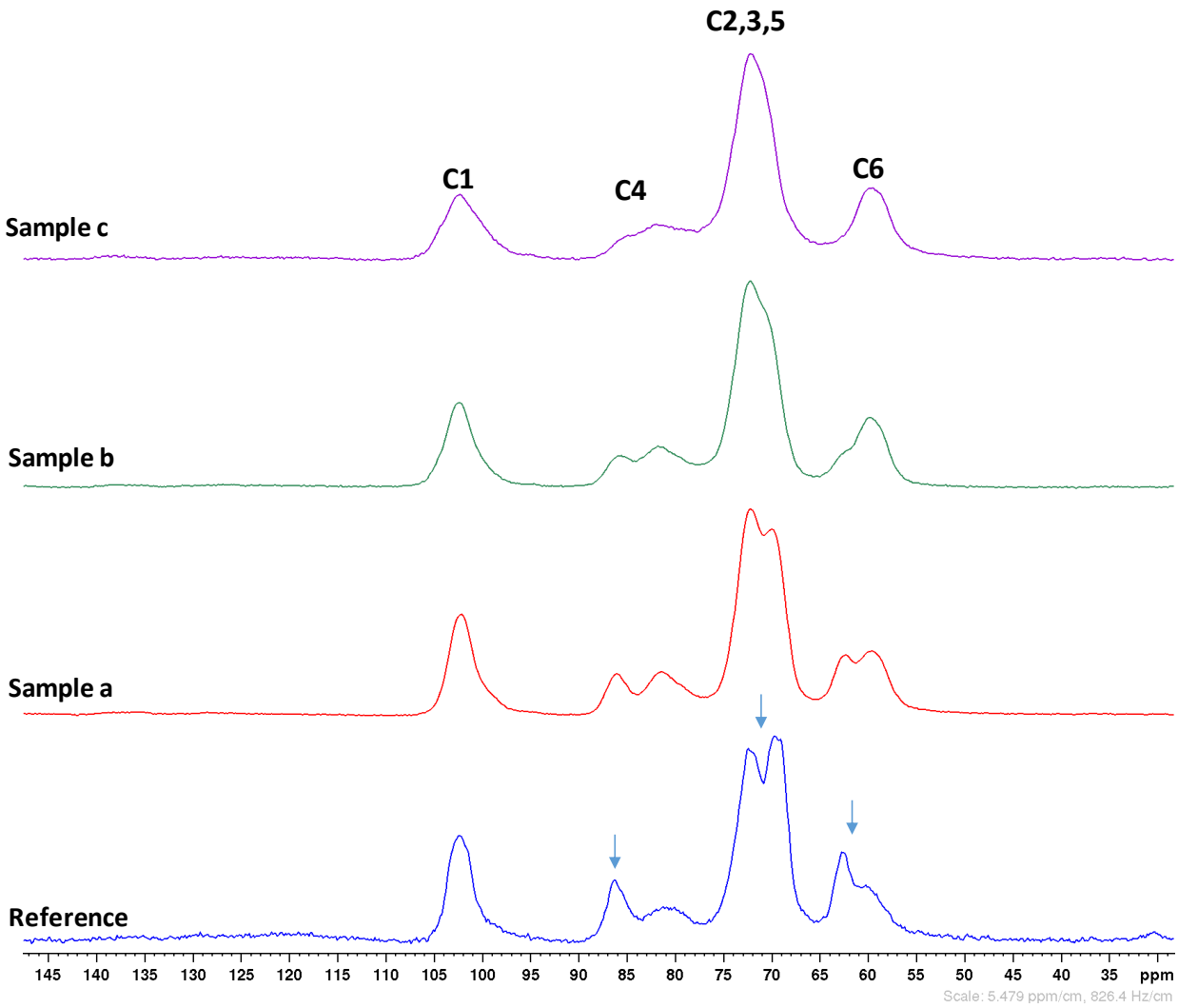
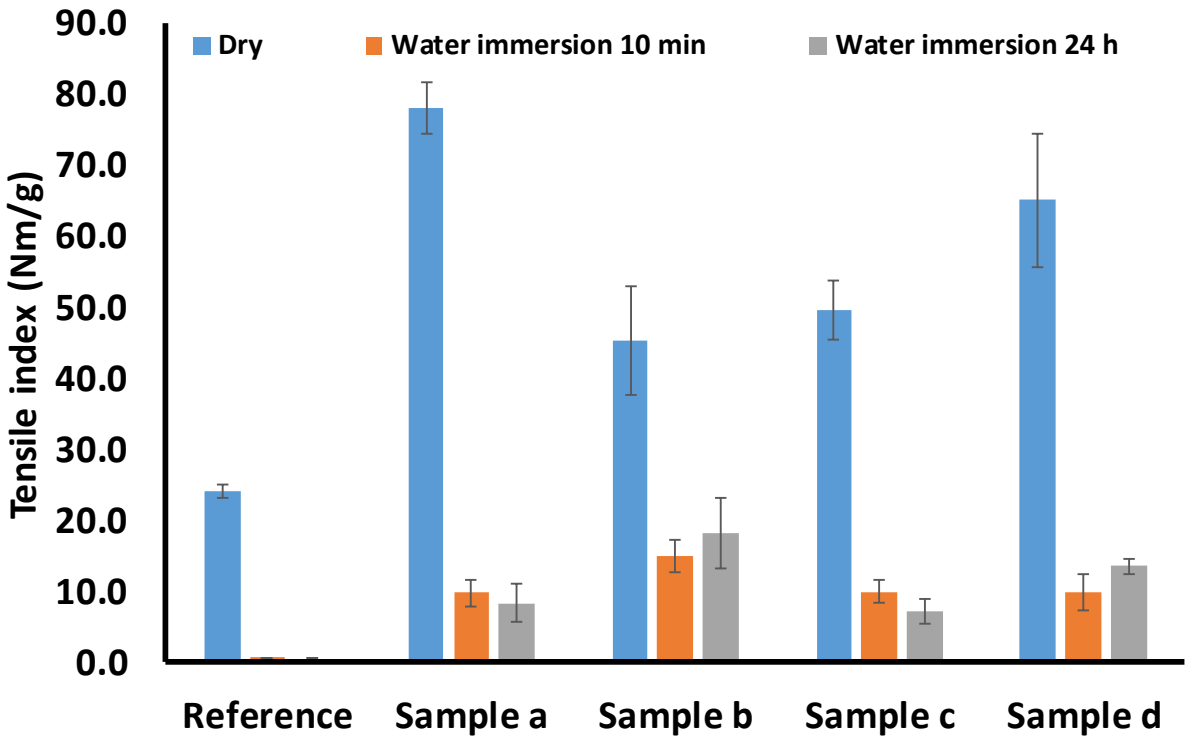


Figure 6. ^{13}C CP/MAS NMR spectra of paper before and after treatment with the "chemical welding" procedure. The arrows above the reference spectrum indicate the regions where the main changes took place.

Mechanical properties of "chemically welded" paper sheets

The prepared samples were studied in detail with typical paper characterization methods (Table 1). The IL treatment significantly increased the mechanical strength of paper. With the mildest treatment conditions (sample a), the dry tensile index value more than tripled from 24.1 ± 0.8 to 78.1 ± 3.6 Nm/g (Figure 7). When more IL and a higher heat activation temperature was used (samples b, c, and d), the tensile index was slightly lower compared to that of sample a. However,

this is only an apparent decrease because in the definition of the tensile index, the force is normalized with the grammage of the paper, which increased. The wet strength of the paper was drastically increased already with the mildest treatment conditions (sample 2, wet strength 8.36 ± 2.59 Nm/g, 24-hour immersion in water). The highest wet strength values (18.23 ± 4.97 Nm/g) were achieved with sample b. The transparent samples (sample c and d) had slightly lower wet strength values. The wet tensile strength retention of sample a was 10%, and with more severe treatment conditions (samples b and d), it increased to above 20%. Sample c had a somewhat lower wet strength retention of 15%, which was mostly caused by the pores left behind by air bubbles formed during heat activation, as seen in SEM images (Figure 5d). The wet strength retention of 20% is comparable to the value reported for regenerated cellulose films made from cotton linters by dissolution to and regeneration from NaOH/urea.[32] The wet strength is increased by the fusion of the fibre surfaces, forming a similar structure as seen in regenerated cellulose films. Earlier, paper has also been treated with undiluted molten [BMIM]Cl, resulting in the dry and wet strength values of 2.8 and 0.38 kN/m, respectively.[28] The values found in this this study (sample b 8.21 and 0.88 kN/m, respectively) were significantly higher. Direct dipping in pure IL mostly affects the surface of the paper, whereas dilution followed by cosolvent evaporation causes a more even fusion of fibre surfaces, because the IL can be transported evenly through the paper structure. This explains why both wet- and dry-strength properties were significantly increased.



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287 *Figure 7. Tensile index (tensile strength normalized by grammage) of the IL-treated sheets measured dry,*
288 *after 10 min, and after 24-h water immersion.*

289 Considering all the mechanical strength data (Table 1), we can conclude that the IL treatment
290 increased the toughness of the paper significantly. This can be seen in the significant increases in
291 the TEA index, the modulus of elasticity, and Scott bond values. However, the IL treatment does
292 not increase the tear index of paper. Analogously, kraft pulp beating results in a paper with a
293 denser structure and a higher tensile strength, but lower tear strength.[5]

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298 *Table 1. Mechanical properties of the IL-treated sheets.*

	Samples				
	Reference	**a**	**b**	**c**	**d**
Grammage, g/m²	96	105	118	211	161
Single sheet thickness, µm	173 ± 5	174 ± 12	187 ± 10	214 ± 18	135 ± 19
Apparent sheet density, kg/m³	557 ± 16	603 ± 40	631 ± 33	988 ± 83	1192 ± 167
Bulk, cm³/g	1.80 ± 0.05	1.66 ± 0.11	1.58 ± 0.08	1.01 ± 0.08	0.84 ± 0.12
Air permeance (Bendtsen), ml/min	3880 ± 197	5720 ± 828	43.3 ± 54.3	7.6 ± 0.3	0.265 ± 0.000
Tensile index, Nm/g	24.1 ± 0.8	78.1 ± 3.6	45.4 ± 7.6	49.7 ± 4.2	65.1 ± 9.5
Stretch at break, %	4.2 ± 0.6	9.2 ± 0.7	4.7 ± 1.3	5.6 ± 2.6	12.0 ± 6.6
Tensile energy absorption (TEA) index, J/g	0.79 ± 0.13	4.90 ± 0.54	1.63 ± 0.70	2.20 ± 1.35	6.83 ± 4.63
Tensile stiffness index, kNm/g	2.62 ± 0.12	3.65 ± 0.16	2.66 ± 0.35	2.55 ± 0.26	2.72 ± 0.27
Modulus of elasticity, N/mm²	1457 ± 69	2200 ± 98	1678 ± 222	2516 ± 259	3244 ± 325
Tensile index after immersion in water, (10 min), Nm/g	0.68 ± 0.06	9.84 ± 1.90	14.91 ± 2.28	9.98 ± 1.57	9.82 ± 2.57
Tensile index after immersion in water, (24 h), Nm/g	0.56 ± 0.06	8.36 ± 2.59	18.23 ± 4.97	7.25 ± 1.68	13.52 ± 1.18
Tear index, mNm²/g	12.9 ± 2.9	11.1 ± 1.9	7.9 ± 0.7	14.7 ± 0.8	3.1 ± 2.3
Internal bonding strength (Scott bond), J/m²	121 ± 10	>1996	>1996	>1996	>1996

299

300 **Barrier properties of the IL-treated papers**

301 Paper is one of the most common packaging materials, but it cannot fully replace plastic film
302 materials due to its low water resistance and oxygen permeability. Thus, we tested if our
303 "chemically welded" paper could have better barrier properties. For our samples, the air
304 permeabilities were: reference (3880 ml/min), samples a (5720 ml/min), b (43.3 ml/min), c (7.6
305 ml/min), and d (0.265 ml/min). For the detailed water vapour and oxygen permeability and
306 grease barrier characterizations, we selected sample d. As a reference, we measured commercial
307 cellophane and LDPE films. The "chemically welded" paper (sample d) has a rather high water
308 vapour permeability when compared to the commercial materials tested (Table 2). Cellulose is a
309 hygroscopic material, which explains why also cellophane shows a rather high water permeability
310 value compared to LDPE. The oxygen permeability of sample d was significantly lower compared
311 to commercial references. In the grease barrier test of sample d, the grease did not leak through
312 the sample at all. In summary, the IL-treated paper has good oxygen and grease barrier
313 properties, but it transmits water vapour significantly. Therefore, it may be used in applications

in packaging where a water-resistant material with good oxygen barrier properties is required, but a water vapour barrier is not required.[33] Furthermore, as an additional benefit, as an all-cellulose structure that is fully biodegradable, the accumulation of the prepared all-cellulose material in nature is prevented.

Table 2. Water vapour permeability (100/50% RH) and oxygen permeability at 0% RH and 80% RH of the IL-treated paper (sample d). Commercial cellophane and polyethylene (LDPE) are measured for reference.

	Water vapour permeability, 23 °C, (g x µm/m^2 x day x kPa)	Oxygen permeability, 23 °C, cc x µm/m^2 x day x kPa	Oxygen permeability, 23 °C, cc x µm/m^2 x day x kPa	Grease permeability through the sample
Sample d	51842 ± 3141	<0.01	5.1 ± 1	None
Cellophane	12553 ± 71	<0.01	69 ± 1	Na.
Polyethylene (LDPE)	42 ± 4	2180 ± 10	2180 ± 20	Na.

CONCLUSIONS

In this study, we investigated the "chemical welding" of paper by IL by using a two-step process where the IL is transported into the paper structure with water. Dissolution is achieved by heat activation where water evaporates and fibre surfaces are dissolved in the IL. The solvated cellulose can diffuse as a liquid, embedding the still undissolved parts of fibres into a matrix of regenerated cellulose. We conducted a full set of industry-standard paper tests to evaluate the industrially relevant properties of the material. Both the dry and the wet strength of the paper structure is improved. The treatment conditions can be adjusted to produce paper-like materials or regenerated cellulose films. The most severe conditions produce films that are fully transparent and have excellent oxygen and grease barrier properties. As an all-cellulose composite, the "chemically welded paper" can be a biodegradable alternative to fossil fuel-based plastics in applications that can accommodate its high water vapour permeability.

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Author Contributions

The manuscript was written through contributions of all the authors. All authors have given approval to the final version of the manuscript.

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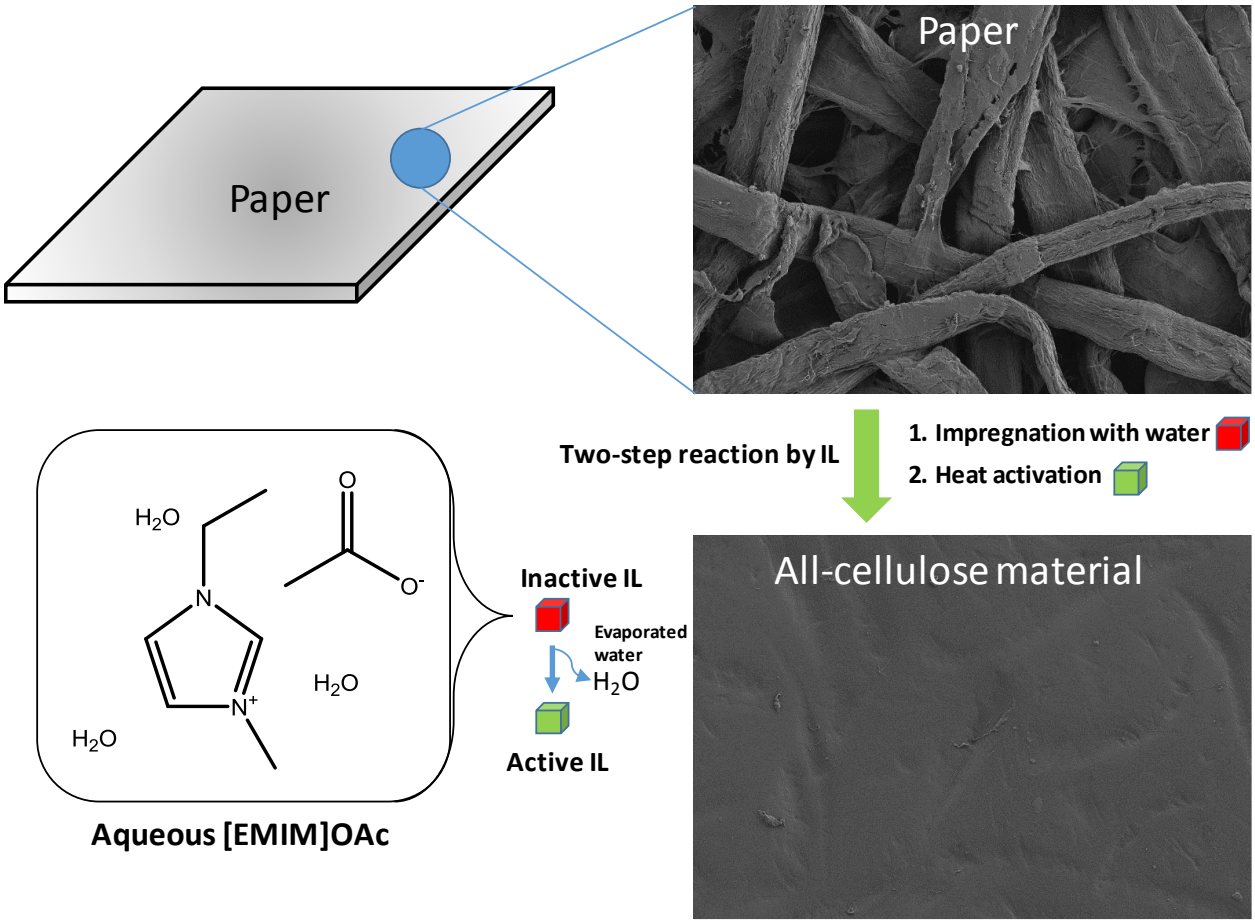
409 **Graphical abstract**



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411

412 **Highlights**

413 • Two-step partial dissolution reaction with [EMIM]OAc was used to transform paper to
414 permanent all-cellulose material.

415 • Water was used to ease the penetration of [EMIM]OAc into paper structure.

416 • Heat activation enabled IL by evaporating water causing effective dissolution of fibre
417 surfaces whose were merged after purification and water evaporation.

418 • Method caused even reaction through the cross-section of paper.

419 • Treated paper has both high dry and wet strengths, and good barrier properties.

420